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Project Summary

Report on Decontamination of PCB-Bearing Sediments

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Polychlorinated biphenyls (PCBs) exist as contaminants in sediments throughout the country. Conventional and emerging waste management methods have not addressed decontamination of these sediments.

EPA has initiated a program to identify chemical/biological methods as alternatives to incineration and chemical land disposal for cleanup of PCB-contaminated sediments. The overall objective of the program is to identify, validate, and demonstrate effective and economical chemical/biological processes for removal/destruction of PCBs in sediments. This report summarizes progress on chemical/biological methods for the detoxification/destruction of PCBs in sediments.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Polychlorinated biphenyls (PCBs) were widely used as a dielectric fluid in transformers and capacitors as well as in hydraulic and heat-transfer fluid systems because of their stability and heat resistance. During the 50 years that PCBs were manufactured and used in this country, an estimated 400 million pounds of these chemicals entered the environment. Because of the broad use of PCBs (ranging from transformer dielectric oils to carbonless paper production), they are widespread in the modern environment, especially the aqueous environment.

Although PCBs are a suspected carcinogen, their acute toxicity is considered to be non to slightly toxic by the LD50 Method. A more significant health impact has been linked to the incomplete combustion (burning) of PCBs. Under certain circumstances, oxidation of PCBs form dioxins and furans, most toxic of all man-made substances. While PCBs have long been known to be toxic, they have only recently been acknowledged to be a general threat to the environment. The characteristics that made PCBs such a problem is their stability and therefore, persistence in the environment. These chemicals have been found in measurable concentrations in waterways and sediments through the world and are widely spread contaminants of fish and wildlife resources. PCB contamination began in an era when industrial wastes were disposed of by flushing them directly into waterways, local sewage plants or landfills.

The PCB contamination problems in New Bedford, Massachusetts (EPA Region I), the Hudson River in New York (EPA Region II), and in Waukegan, Illinois (EPA Region V) are reported to be the worst in the United States in terms of concentration and total quantity of PCBs. It is estimated that 290,000 kg of PCBs are contaminating 382,000 m^3 (500,000 yd^3) of sediments of the Hudson River. During the 1970's approximately 907,000 kg of PCBs were used in the New Bedford area annually, of which an estimated 45,500 kg were improperly disposed. Also, there are many industrial lagoons contaminated with large quantities of PCBs. For example, EPA Region III reports three sites in

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Pennsylvania and two in West Virginia where over 3200 m^3 (2447 yd^3) of soil sediments are contaminated with PCBs. The PCBs contamination problems pose threats to both drinking water and the fishing industry.

The only available proven technology is dredging and expensive incineration. Land disposal of the untreated sediments has legal restrictions. Biodegradation is a possibility, but sufficient information does not exist to design and operate such a system. There is little experience in the application of encapsulation technology to PCB-contaminated sediments.

Although a great amount of work has been done by many research groups in the area of PCB-contaminated liquids, relatively little effort has been directed toward PCB-contaminated sediments and sludges. The EPA Regional and Program Offices are being asked to comment on the technical and economic feasibility of chemical biological processes for cleanup of these sediments and sludges. These Offices do not have adequate data to recommend any of a number of processes proposed or being tested evaluated for the decontamination of sediments containing PCBs.

Assessment of Processes

Because there is little known about the application of chemical and biological processes to the decontamination of PCBs in sediments, Research Triangle Institute (RTI) was engaged by EPA to undertake a study to identify the most technically feasible processes that have been proposed by research concerns for the removal of PCBs from sediments, to identify their extent of development, effectiveness, limitations and probable costs, and to determine needs for their further development. The study involved three phases: identification of the most promising processes and their further development needs; evaluation of the unit operations involved in the processes against engineering, health, and environmental criteria for further testing and evaluation; and definitive assessment of the recommended treatment processes using pilot systems and contaminated sediments.

The first phase involved four steps: data acquisition, screening and selection of most technically feasible processes, development of criteria for process assessment, and process assessment. Under step one, three major sources of data were: EPA's file of proposals and correspondence concerning problems of PCB contamination and possible approaches to alternative solutions; the open literature; and direct contacts with proponents of treatment technologies. In step two, the processes were categorized according to their generic technology so that their potential performance could be judged appropriately. Processes with undesirable aspects, for example lack of tolerance for water, were rejected from further assessment. Criteria for assessment, step three, were chosen which relate to a broad range of principles of operation of diverse applied technologies, yet can be used effectively in comparing one treatment process with another. Additional factors, specific to a technology, were included to help portray the inherent strengths and limitations of a process. The seven criteria used and three additional factors were: estimated residual PCB; available capacity; conditions limitations; concentration range handled; status of development; test and evaluation data needs; estimated cost; unit operations; RCRA waste generated; and estimated destruction detoxification removal efficiency. In the final step, the processes were assessed by characterization and ranking. Characterization provided for objective comparison of the processes. Ranking provided a subjective comparison of the processes based on the seven criteria.

In the first phase, eleven emerging alternative treatments of the sixty-four processes considered for PCB-contaminated sediments were compared and ranked. Eight candidate treatment processes showed potential as alternatives to chemical waste landfill and to incineration. Some had been tested on soils but none were tested specifically on PCB-contaminated sediments. Sediments of concern differ from soils in several properties that influence the performance of unit operations involved in the treatment processes.

The second phase built upon the first phase of the assessment so that EPA may have more complete information before evaluating any technology in the field. This second phase involved three steps: consulting with the treatment process developers; technical assessments of the process; and the selection of three of the processes for thorough test and evaluation. Consultations included visits to the developers' facilities where further information was developed. The most recent performance data were reviewed. The availability of the system was determined. The visits included a checklist of needed information and criteria for assessment of the processes. The technical assessment was based upon the projection of the performance and cost of a large-scale treatment system of sufficient capacity to treat an estimated 380,000 m^3 of PCB-contaminated Hudson River sediments in 2.5 years. Specific sample data from Hudson River sediments were used to guide the projection of operating conditions required for treatment by each process assessed. The processes were compared and rated using the results of the assessment. Based on composite ratings, three processes showing the highest rating were recommended for test and evaluation.

The objective of the proposed third phase is to provide EPA with a defensible thorough test and evaluation of the three alternative treatments selected in Phase 2. In carrying out this phase, EPA will arrange to have PCB-contaminated sediments treated in pilot-scale processing systems selected in Phase 2. The pilot tests will evaluate performance under field conditions, and will be supported by laboratory tests. Confirmation of treatment process effectiveness will make these processes very viable and cost-effective methods of treating these hazardous wastes.

The following processes were studied by RTI on Phase 2 of the study:

B.E.S.T.

The Basic Extraction Sludge Treatment (B.E.S.T.) process was developed by the Resources Conservation Co. (RCC) 3101 N.E. Northup Way, Belleview, WA 98004. The process uses a solvent having an inverse critical solution point in water to remove water and oily material from solid matter. It has been applied to cleanup of PCB-contaminated oily sludges at a CERCLA site (Savannah, Georgia).

Ultrasonics/Hydrogen - Ozone/UV Technology

The process is based upon simultaneous extraction and treatment of a sediment slurry with ultrasound (above 20KHz) added to increase rates of dissolution of the PCB contaminants and reduce coalescence of bubbles of gas reactants. The treatment is achieved by either ozone ultraviolet irradiation or hydrogen ultraviolet irradiation. The sediments are fed as a slurry containing about 20 wt. percent solids into a mixing tank where predetermined amounts of detergent and sodium hydroxide are

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added. The conditioned mix is pumped to the reactor where the solids are maintained in suspension while the mixture is exposed to ultraviolet irradiation and ozone (or hydrogen) is added. During this treatment, microscopic turbulence is produced through ultrasonics. The treated slurry is fed into a cyclone where the solids are removed, sampled, and tested to certify them for discharge. The separated water is neutralized and also tested before discharge.

Bio-Clean Naturally-Adapted Microbial

The Bio-Clean Naturally-Adapted Microbial process has been developed by Bio-Clean, Inc. Bio-Clean is a company engaged in developing process systems to clean up, remove or destroy hazardous chemicals in the environment. The process utilizes *Arthrobacteria sp* and or other naturally-adapted microbes to destroy PCBs (and related organics) under aerobic conditions.

KPEG with DMSO

Nucleophilic substitution with the KPEG process and the Galson Research version (Terraclean-CI process) was looked at as a means of decontaminating PCB-bearing sediments. The potassium polyethylene glycolate (KPEG) process has two potential applications in the treatment of PCB-contaminated sediments: the treatment of the sediments themselves, or the treatment of concentrated PCBs resulting from extraction processes. The former is assessed in terms of the Galson Modified KPEG process, that is, with dimethyl sulfoxide (DMSO). The latter application would require treatment of a relatively concentrated solution of PCBs in a non-aqueous solvent (triethylamine, kerosene, etc.)

CFS Propane Extraction

The CFS Propane Extraction Process is a technology available from C. F. Systems Corporation, 25 Acorn Park, Cambridge, Massachusetts 02140. The company is a subsidiary of Arthur D. Little. As applied to PCB-contaminated sediment, the process uses propane at ambient temperature and 1378 kPa (200 lb/in^2) to extract PCBs along with other oily organics from a water slurry of the sediment. The treated slurry is discharged after separation from the liquid propane which contains dissolved contaminant. The propane solution is fed to a separator where the solvent is removed by vaporization and recycled. The contaminants are drawn off as a concentrate for final treatment. The process has been tested for PCB-containing refinery sludge. The PCB content of the solids component of the sludge was reduced to 5 ppm.

Modar Supercritical Water - Oxidation

This process has been developed by MODAR, Inc., 3200 Wilcrest, Suite 220 Houston, Texas 77042. The process utilizes water above critical conditions (374°C and 22.1 MPa) to increase the solubility of organic materials and oxygen and effect a rapid oxidation, destroying organic contaminants. It has been applied to destroy PCBs in oils, and to decontaminate dioxin tainted soil. The company has a laboratory test unit and skid-mounted pilot test unit having a nominal organic material flow capacity of 190 liters/day. This unit has been operated at MODAR's research facility in Natick, Massachusetts and at the CECOS International Niagara Falls site.

In Situ Vitrification

In Situ Vitrification was previously discussed as a process developed to treat radionuclide-contaminated wastes, and subsequently tested for possible adaptation to the treatment of PCB-contaminated soils. Submerged sediments would be dredged before treatment. The process stabilizes contaminated soils by melton into a durable glass and crystalline form. Four electrodes are inserted into the sediments in a square array. A path for electric current is made by placing a mixture of graphite and glass frit between the electrodes. Dissipation of power through the starter materials creates temperatures high enough to melt a layer of sediment, which establishes a conductive path. The molten zone grows downward through the contaminated soil. At the high temperatures created (< 1700°C), organic materials pyrolyze, diffuse to the surface, and combust. Off-gases are collected, monitored, and treated.

Solvent Extraction Process

In a separate study, scientists at the New York University's Department of Applied Science have been carrying on a three year EPA supported investigational program on the development and evaluation of a low energy process technology for the solvent extraction and subsequent chemical destruction of PCBs from contaminated sediments and sludges. This is also one of the processes which was assessed by RTI in Phase 2. This program involves experimental studies on potentially more cost-effective PCB disposal alternatives to currently accepted practices. The research activities during the first year of this program comprised the investigation of suitable solvent extraction and supporting equipment, identification of candidate solvents for extraction and concurrently developed application and verification of analytical methodology for quantitative determination of PCBs in contaminated sediments. Exploratory experiments were also carried out on the extraction of PCBs from contaminated sediments obtained from Waukegan Harbor, Illinois.

The concept of using kerosene as an extraction solvent for removing PCBs from sludges and sediments was based on two factors: (1) the low cost of kerosene and (2) some work conducted on extraction of PCBs from soils (M. B. Saunders at Oak Ridge National Laboratory, 1985). While the cost factor is a driving force in any development, it alone cannot overcome technical impracticalities. It became quite evident early in this study that the presence of large quantities of water in the contaminated samples presented an insurmountable barrier to the use of kerosene in this application. A new approach to this difficult problem was needed and is herein presented.

The first step of the process takes advantage of the extremely low solubility of PCBs in water. In a typical PCB-contaminated sediment or sludge composed primarily of water with generally 20% total solids, virtually all of the PCBs are associated with the sediment. Thus, the first processing step is a physical separation of water and solids. In the second step, the PCB-contaminated oil is dissociated from the sediment substrate. This is accomplished by a multi-stage counter-current leaching with a hydrophyllic solvent. The third step is a stripping operation in which the PCB-containing stream from above is contacted in a liquid-liquid extractor with a hydrophobic solvent and additional water. The two streams which leave this step are the PCBs concentrated in stripping solvent which proceeds to appropriate methods for final destruction, and the hydrophyllic

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solvent water mixture containing trace PCBs. The solvent water mixture goes next to a distillation column in which the solvent is separated and returned to the leaching process. The water contaminated with trace amounts of PCBs is recycled to the front of the stripping process to close the cycle.

Conclusions

Various experimental and supporting activities were carried out during the first year of the EPA-supported research in order to develop an adequate data base for achieving an effective low energy process for the extraction of PCB's from contaminated sediments and sludges. Achievements from these investigations are summarized as follows:

1. Selection of extraction and supporting equipment for a specific extraction.
2. Identification of candidate solvent systems for extraction.
3. Development of an appropriate analytical methodology for the determination of PCBs in contaminated sediments and sludges.
4. Development of an innovative process scheme for the extraction of PCBs from sediments and sludges.

Emerging treatment processes for decontamination of sediments containing PCBs that show potential as alternatives to incineration and chemical waste landfill have been identified in Phase 1 of an assessment study. Eleven alternative treatments were compared and ranked using technical performance, status of development, test and evaluation data needs, and cost as factors. The first eight processes show potential for reduction of PCB concentrations to the desired background levels (1-5ppm) or less, with minimum environmental impacts and low to moderate cost. The sediments must be dredged for application of these treatments. Based on the weighted ratings of Phase 1, eleven processes ranked as follows from highest to lowest: KPEG, LARC, Acurex, Bio-clean, Modar-Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006.

At the start of the final assessment study before field tests, some former developers indicated their processes should not be considered, and some new processes became available. Thus, in the next assessment study-Phase 2, eight emerging treatment processes for decontamination of PCB-contaminated sediments were evaluated as candidates for thorough test and evaluation using a test system of sufficient size to provide performance, cost, and scale-up data for a large commercial plant. The processes assessed and listed in relative desirability of test and evaluation include: (1) Basic Extraction Sludge Treatment (B.E.S.T.) developed by Resources Conservation Co.; (2) UV Ozone or Hydrogen Ultrasonics Technology of Ozonic Technology, Inc.; (3) Bio-Clean Naturally-Adapted Microbial Process of Bio-Clean, Inc.; (4) KPEG (Galson) Process modified by Galson Research Corp.; (5) Low Energy-Acetone-Kerosene Extraction Process developed by the Applied Science Dept. of New York University; (6) Modar Supercritical Water Oxidation Process of Modar, Inc.; (7) CFS Propane Extraction Process of C. F. Systems and (8) In-Situ Vitrification Process by Battelle Pacific Northwest Research Laboratories.

Recommendations

While all the processes except In Situ Vitrification appear to merit further development for this application, those three with the highest comparative ratings are recommended for EPA-supported thorough test and evaluation. These are the Basic Extraction Sludge Treatment, UV Ozone or Hydrogen Ultrasonics Technology, and Bio-Clean Naturally-Adapted Microbe processes.

There is in an evaluation of processes such as this, much uncertainty. Additional research of the other processes is very important to fill in the data gaps. The other processes, for example, may be more cost effective on a smaller scale than what the study assumed or with other unit processes. The results of the EPA funded study at the New York University have led to a novel approach to treatment of PCB-contaminated sediments and sludges. It is recommended that a study is needed to model, engineer and otherwise fully characterize this process so that its full potential might be realized.

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The complete report, entitled "Report on Decontamination of PCB-Bearing Sediments," (Order No. PB 88-113 220 AS; Cost: $14.95, subject to change) will be available only from:

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